Identification and Comparison of Solvents and Paint Removers as Alternatives to Methylene Chloride in Paint Removal Applications

R&D, W. M. Barr
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ABSTRACT

This study compares the paint removing performance of methylene chloride to 22 solvents currently used in non-methylene chloride paint removers or solvents proposed as an alternative to methylene chloride by chemical manufacturers. The paint stripping performance of three methylene chloride paint removers was then compared to 26 non-methylene chloride paint removers and five experimental formulas using alternative methylene chloride chemistry. The solvents and paint removers were tested on 1 month and 1 year aged wood panels treated with multiple layers of an oil-based alkyd paint, a solvent-borne epoxy paint and OEM automotive coating. For chemically resistant oil-based alkyd, solvent-born epoxy paints and OEM automotive coatings, only methylene chloride based paint removers were determined to be effective.

BACKGROUND

Methylene chloride has been the preferred solvent for use in paint removers for seventy years. Before methylene chloride was introduced, most paint removers consisted of a mixture of benzene and other volatile solvents such as methanol, acetone, and methyl ethyl ketone. Paint removers formulated with these volatile solvents are extremely flammable and the flammability of these paint removers resulted in fires causing injury and deaths. The benzene based removers were rapidly replaced with the methylene chloride paint removers because methylene chloride paint removers can be formulated to be non-flammable and are effective in removing multiple layers of paint. The physical characteristics give the methylene chloride molecule the ability to quickly penetrate multiple layers and to soften or dissolve chemically resistant coatings. Methylene chloride does not deplete the ozone layer and is considered to make negligible contributions to smog formation, the green-house effect and acid rain. Like other organic solvents, methylene chloride can be harmful to human health if used improperly.

Consumer Use of Paint Removers

Most consumers use paint removers for refinishing antique furniture, or woodworking's (doors, frames, moldings, etc.) in older houses. Many of these items have been painted, and repainted many times over the years. This results in items having multiple layers of paint containing different chemistry types and a different degree of difficulty from being removed. Paint removers are also used in the auto body repair industry to help with vehicle restoration.

Effect of Paint Chemistry and Age of Paint

There is a range of paint types that a consumer can encounter when paint stripping. The main paint chemistries that can be encountered include latex, urethane, 1-part epoxy, 2-part epoxy, enamel (alkyd type), lacquer, varnish, and shellac based paint. In recent times, latex paint has taken over the painting industry as the paint technology of choice. This paint is relatively easy to remove with paint strippers, but is also a paint technology that people will not frequently encounter as they are stripping older items. Historically, enamel alkyd based paint have been the most prevalently used paint technology. The resin used in alkyd paint dries by an oxidation reaction with oxygen from the air after the solvents has evaporated from the paint. The oxidation reaction irreversibly cross-links the polymers hardening the alkyd resin making it very difficult to remove. The alkyd paint continues to form cross-linking bonds as the paint ages making older painted items even harder to strip. 2-part epoxy paint is by far the most difficult paint technology to remove. It is frequently used in industrial settings. For this reason, the

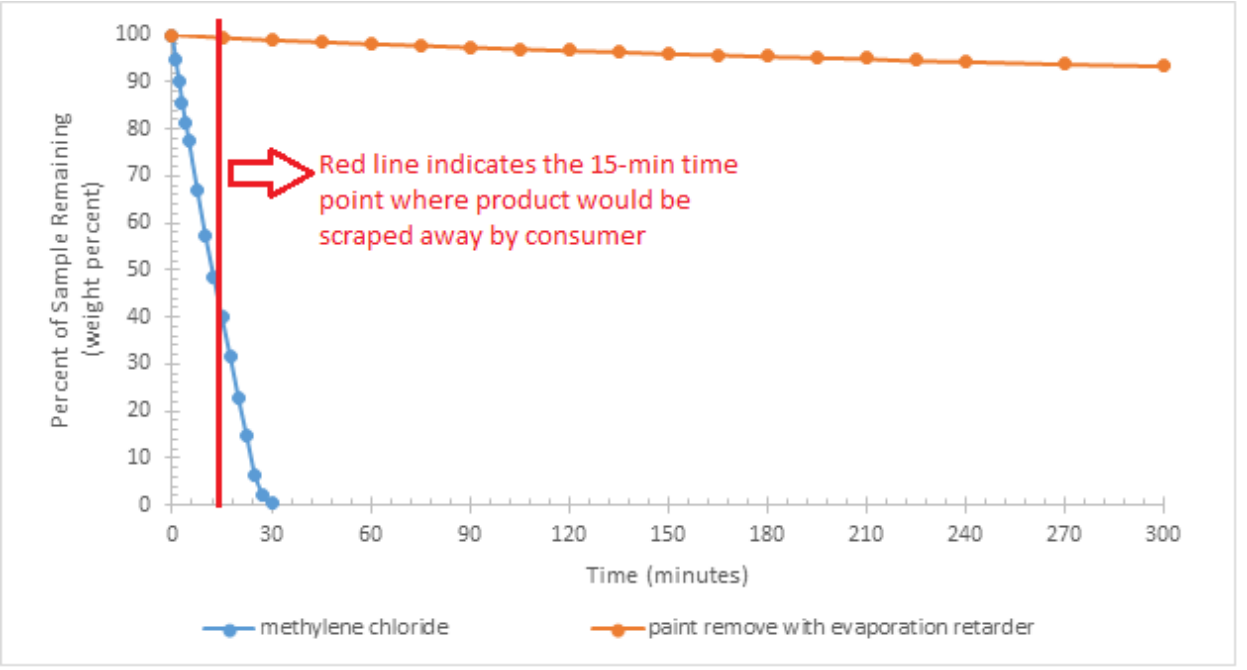
experimental studies outlined in this report will focus on the removal of alkyd, 2-part epoxy paint, and OEM automotive coatings.

Basics of Paint Remover Formulation

A chemical paint remover is composed of a mixture of solvents, additives and sometimes an activator. To be an effective paint remover, the solvent must be able to penetrate multiple layers of paint and have solubility to cause the paint to swell which breaks the bond of the paint to the substrate. The movement of the solvent from the paint remover to the paint layer is call diffusion and is the result of the random kinetic movement of the solvent. The rate of diffusion of is affected by the size of the solvent molecule (molar volume) and the polarity of the molecule. Smaller, nonpolar molecules will have a higher diffusion rate into the coating than molecules that are larger or more polar. The more effective replacements for methylene chloride will be molecules with the following general characteristics, small polar or halogenated molecules, five-member cyclic rings or six-member aromatic rings. These types of molecules are generally flammable and will also have health and safety risks.

Additives, such as surfactants, thickeners and paraffin wax are added to modify the physical properties of the paint remover. Surfactants improves the wetting of the surface by the paint remover and permits the use of water for clean-up after the paint has been stripped. Thickeners are added to allow the paint removers to cling to vertical surfaces. To reduce the evaporation of methylene chloride and other solvents in the paint remover, paraffin wax is added. Paraffin wax reduces the evaporation of the solvents by forming a physical barrier between the paint remover and air. The weight loss of methylene chloride over a period of five hours was compared to the weight loss of a paint remover containing more than 60% methylene chloride and an evaporation retarder with the results shown in **Figure 1.** Approximately 20 grams of methylene chloride and 20 grams of the paint remover were placed in separate containers and the weight of the sample remaining was determined at timed intervals. After 30 minutes, only 0.5% of the straight methylene chloride remained in the container. The result of the study showed that evaporation retarder is effective in reducing the evaporation rate of methylene chloride from the paint remover. As shown in **Figure 1**, 98.9% of the paint remover remained after 30 minutes and 93.5% remained after five hours. Since the methylene chloride based paint remover (containing evaporation retardant) is effective after 15 minutes from application, the amount of methylene chloride released into the atmosphere during this time is minimal, minimizing the inhalation risk to the product user. At 15 min, only 0.6% of the methylene chloride based paint stripper formula has evaporated.

Figure 1. Comparison of weight loss of methylene chloride to a methylene chloride paint remover formulated with an evaporation retarder at 70°F. At 15 min, only 0.6% of the methylene chloride based paint stripper formula has evaporated.



To increase the performance of the paint remover, an acid or a base is sometimes added as an activator. The activator is thought to disrupt the bond between the substrate and the paint and weaken or break the chemical or physical bonds in the polymer that is used in the paint. Formic acid, ammonium hydroxide and ethanolamine are common activators used in paint removers.

To establish the performance criteria of methylene chloride based paint removers, the label copies from different manufactures were evaluated for consumer benefits. The three most important criteria include:

A. Fast removal of the coating, starts working within 15 minutes.
B. Removal of many types of coatings including oil-based and epoxy paints for architectural coatings and factory applied OEM automotive paints
C. Removal of multiple layer of coatings

Other criterial considered in the evaluation of the paint remover includes the cost of the paint remove and the VOC content of the paint remover. The VOC content of paint removers is limited to 50 % by weight. When considering viability of a paint remover it must be considered that the paints to be removed are generally older and more chemically resistant than many paints available today. While water-based latex paints are widely available and chemically easily removed, they were not nearly as common 30 or more years ago. Furthermore, there are coatings in common use today that are

considered more chemically resistant than water-based latex paints. Once again, this study focuses on the more difficult, chemically resistant oil-based alkyd and solvent-born two-part epoxy paints.

MATERIALS AND METHODS

The procedure used to test the performance of the solvents and paint removers is based on a modification of the ASTM D-6189 (2003) test method (Standard Practice for Evaluating the Efficiency of Chemical Removers for Organic Coatings). Modification of the procedure included using 12 x 8 inch panels instead of 12 x 12 inch panels and the panels were treated with five coats of the oil-based alkyd paint instead of three coats as described in the panel preparation procedure in the ASTM D-6189 test method. Painted panels aged 1 month were used for screening experiments and painted panels aged 1 year were used for final efficacy validation. The solvents and paint removers were applied to the panel using a pipette instead of following manufactures directions for application as called for in the ASTM test method. During the paint removal step, scrapping was performed using moderate force with a plastic paint scrapper.

Solvent Selection – The solvents used in this study were selected from solvents currently used in non-methylene chloride paint removers, solvents recommended as methylene chloride replacements by chemical manufacturers, and the EPA Exempt VOC Solvents list. Technical grade samples of the solvents were obtained and used in this study's experimental formulations without further purification.

Paint Remover Selection – The paint removers used in this study were purchased from hardware stores or from suppliers on the internet. Composition and the flash point of the paint removers based on information found in the Material Safety Data Sheets (MSDS) are listed in **Appendix A.** All paint removers were used as is in the experiments.

Experimental Paint Removers – Based on the results of the solvents screening testing, two alternative methylene chloride solvents were identified as having some paint remover potential. These solvents were formulated into paint removers that meet the 50 wt% VOC requirements. Three other experimental formulas based on solvent chemistry utilized by paint removers on the market today were also formulated into experimental paint removers with the VOC content less than 50 wt%. These experimental paint removers are listed below:

A. a solvent based remover based on toluene, methanol, and acetone
B. a solvent based remover based on 1,2 trans-dichloroethylene, methanol, and acetone
C. a solvent based remover based on 1,3-dioxolane, methanol, and acetone
D. an emulsion based on benzyl alcohol
E. an emulsion based on dibasic esters (DBE)

Paint Selection - Oil-based alkyd paint was selected to be used since it has historically been the most predominantly used paint technology and consumers are typically stripping older items which contains multiple layers of this type of paint. Two-part component epoxy paint was also selected because it is the most difficult paint technology to remove and is frequently used in industry applications. The paints used were purchased from a local hardware or paint stores. The paints purchased for this study are listed in Table 1 along with numbers of layers of paint used on the test panel. Only one type of paint was used for each test panel.

Table 1. List of paint, paint type and number of coatings used in study

Paint	Paint Type	Number of Coatings
Rust-Oleum Professional High Performance Protective Enamel Exterior Gloss	Oil-based alkyd paint	5
Sherwin Williams Macropoxy 646	Two component oil-based epoxy paint	3

1 Month Aged Panel Preparation Procedure – Sanded birch plywood (4 ft. x 4 ft. x ½ in.) was cut into approximately 12 x 8 inch panels. A four-inch multi-purpose paint roller was used to apply the coats of the designated paint to the birch panels as determined in Table 1. Each layer of paint was dried for four hours at ambient conditions and then was placed in a laboratory oven at 50°C overnight. Each layer of paint was tinted to a different color to increase the visibility of the paint layers. The color schematic went as follows: Blue = color of 1st paint layer applied, White = color of 2nd paint layer applied, Green = color of 3rd paint layer applied, Yellow = color of 4th paint layer applied, Red= last paint layer applied. After the red coat of paint was applied, the panels were then aged for 30 days at 50°C in the laboratory. The test panels were then stored at ambient conditions until needed for the stripping test.

1 Year Aged Panels- Painted panels aged for 1 month/30 days are only good for giving directional data on the efficacy of a paint stripper. These 1 month aged panels are typically used by the formulation chemist to quickly screen new chemistries to see if they have the potential of becoming an efficacious paint remover. The reality is that consumers are trying to remove multiple layers of paint off items that are many years old. As mentioned in the introduction, alkyd paint types get harder to remove over time due to their chemistry. True efficacy validation of a paint remover requires it to be tested on Alkyd painted boards that have been allowed to age for at least 1 year. These boards were initially prepared in the same manner as the 1 month aged boards, but were allowed to sit at ambient conditions for up to a year prior to testing.

Automotive Panel Preparation – The hood from a 2006 Chevrolet Impala SS was purchased in good condition with the factory paint intact. The hood was cleaned with a damp cloth and used in testing without further modifications. The original paint was used on the hood, so the paint job during removal testing was at least 9 years old. The age of this paint is not as of great importance due to the chemistry being stable over time in comparison to the Alkyd paint which continues to react and get stronger.

Neat Solvent Screening – Neat solvent screening was done on 1 month aged boards to generate directional efficacy data on chemicals that might be promising to be incorporated in a paint remover formula. A grid is marked on the panel with masking tape creating test cells approximately 1 ½ in. x 1 ½ in. for the stripping trials. Each cell was labeled with the name of the solvent to be tested and the duration time of the test. A C31 Large Commercial Sponge from 3M was cut to approximately sized 1 ½ in. x 1 ½ in. x ¼ in. pieces were placed on each test cell to control evaporation and retain the solvent to the test area. For each sample, 2 ml of solvent was applied to the sponge and a timer is started. Additional solvent was added to the sponges as needed to ensure that the solvent remained in contact with the surface of the test panel. At the timed intervals, the test area was scraped using a plastic scraper and evaluated for the effects on the coatings and the number of layers of paint removed.

Experimental Paint Remover Screening and Validation – Experimental paint remover formulas were tested on 1 month aged boards to get directional efficacy data in comparison to a commercialized paint remover competitive set. This process helps weed out underperforming formulas prior to testing on valuable 1 year aged boards. This same experiment was then repeated on 1 year aged alkyd painted boards to validate the true efficacy of the experimental and commercially available paint removers. A grid was marked on the panel with masking tape to create test cells of approximately 1 ½ in. x 1 ½ in. dimensions. Each cell was labeled with the name of the solvent to be tested and the time duration of the test. Approximately 2 ml of the paint remover was applied to the cell and a timer is started. At timed intervals, the test area was scraped using a plastic scraper and judged for the effects on the coating and the numbers of layers of paint removed.

Results

Neat Solvent Screening – Neat solvent experiments were done on 1 month aged painted boards for the sole purpose of getting directional efficacy data to drive future non-methylene chloride formulation development. The results comparing the performance of methylene chloride to the 22-alternate solvents selected are listed in Table 2. The performance was evaluated after 15 minutes, 30 minutes and 1 hour with number of layers of paint removed and the effect of the solvent on the paint noted. Methylene chloride performed the best removing all five layers of oil-based alkyd paint and two layers of the two-component oil-based epoxy paint in 15 minutes. Trans-1,2-dichloroethylene and 1,3-dioxolane were identified as the best performing alternate solvent removing all five layers of the oil-based alkyd paint in 30 minutes. After 1 hour, 1,3-dioxolane removed two layers of the two-component oil-base epoxy paint, however, trans-1,2-dichloroethylene failed to remove any layers of the epoxy paint after an hour. Results from this experiment helped drive decisions on which chemicals could be used in new experimental paint removal formulas that did not utilize methylene chloride.

Table 2. Neat solvent experiments were done on 1 month aged painted boards for the sole purpose of

Chemical (Neat)	Alkyd (5 Layers)			Epoxy (3 Layers)		
	15 min	30 min	1 hrs	15 min	30 min	1 hrs
methylene chloride	5	5	5	2	2	2
trans-1,2 dichloroethylene	5	5	5			
1,3 dioxolane	5	5	5			2
n-methyl-2-pyrrolidone		5	5			
acetone	5	5	5			
dimethoxymethane (methylal)		5	5			
n-butyl propionate			5			
dimethyl sulfoxide (DMSO)			4			
dimethyl carbonate						
benzyl methyl ether						
TOC (2,5,7,10 tetraoxaundecane)						
3-methoxy-3-methyl-1-butyl acetate (MMB-AC)						
Steposol MET-10U						
PCBTF/Oxsol 100						
3-methoxy-3-methyl-1-butanol (MMB)						
Eastman Omnia (butyl-3-hydroxybutyrate)						
benzyl alcohol						
dibasic esters (LVP)						
dibutoxymethane (butylal)						
propylene carbonate						
Elevance Clean 1200						
soya methyl ester						
glycerol formal						

no effect on coating	
slight softening of paint but no removal with plastic scraper	
paint has softened requiring effort to remove with plastic scraper	
paint has blistered with all layers paint removed with plastic scraper	

getting directional efficacy data to drive future formulation development. Results of solvent testing showing the layers of oil-based alkyd and two component oil- based epoxy removed.

The performance of trans-1,2-dichloroethylene and 1,3-dioxolane in removing OEM automotive paint was then compared to methylene chloride and three solvents n-methyl-2-pyrrolidone, benzyl alcohol and DBE currently used in commercially available non-methylene chloride paint removes with the results listed in **Table 3.** The performance of the solvents was evaluated after 15 minutes, 30 minutes, 1 hour and 4 hours with number of layers of paint removed and the effect of the solvent on the paint noted in **Table 3.** Once again methylene chloride performed the best by removed the clear and color coat in fifteen minutes. Trans-1,2-dichloroethylene and 1,3-dioxolane removed the clear and color coat after 30 minutes while NMP, benzyl alcohol and DBE had no effect on the paint after four hours. None the neat solvents, including methylene chloride, stripped all layers of the automotive coating including the primer. Only a formulated paint remover would remove all layers of an automotive coating.

Table 3. Results of solvent testing showing the layers of OEM automotive paint removed.

Chemical (Neat)	Automotive Coating			
	15 min	30 min	1 hrs.	4 hrs.
methylene chloride				
trans-1,2 dichloroethylene				
1,3 dioxolane				
n-methyl-2-pyrrolidone				
benzyl alcohol				
dibasic esters (LVP)				

No effect	
Stripped clear coat and top coat	
Stripped clear coat, top coat and base coat	

Experimental Formula Paint Remover Screening on 1 month Aged Boards

Experimental paint remover formulas were tested on 1 month aged boards to get directional efficacy data in comparison to a commercialized paint remover competitive set. This process helps weed out underperforming formulas prior to testing on valuable 1 year aged boards. Test results comparing the performance of three methylene chloride paint removers to 5 experimental formulas and 26 commercial non-methylene chloride paint removers on one month aged boards are presented in **Table 4**. The panels used in this experiment were evaluated after 5 minutes, 15 minutes, 30 minutes, 1 hour and 4 hours with the numbers of layers of paint stripped by the paint remover recorded. For test panels

painted with oil-based alkyd paint, two of the three methylene chloride paint removers, Klean Strip Aircraft Remover and Klean Strip Premium Stripper, stripped all five layers of the alkyd paint after five minutes. The third paint remover, Klean Strip Strip-X, contains less methylene chloride and took 15 minutes to strip the five layers of the alkyd paint. Experimental Formulas A, B, and C were also able to strip all five layers of the oil-based alkyd paint in 15 minutes. Experimental Formula A was formulated with toluene, methanol and acetone. Experimental Formulas B and C contained the two alternate solvents identified in the alternated solvent study and were formulated with 1,2 trans-dichloroethylene, methanol, and acetone and 1,3-dioxolane, methanol, and acetone. Experimental Formula D based on a benzyl alcohol emulsion and Experimental Formula E based on a DBE emulsion failed to strip any layers of the alkyd paint after four hours. Fifteen of the twenty-six commercial non-methylene chloride paint removers tested stripped all layers of alkyd paint in four hours. Eight of sixteen paint removers that stripped the alkyd paint were formulated with NMP. Five of the sixteen paint removers were formulated for professionals to remove automotive or aircraft coatings were based a blend of solvents and high levels of an activator. The remaining two formulas were based on dimethyl sulfoxide (DMSO) or caustic.

For the panels painted with the two-component oil-based epoxy paint, two of the three methylene chloride paint removers, Klean Strip Aircraft Remover and Klean Strip Premium Stripper, stripped two layers of the epoxy paint after 15 minutes. The third paint remover, Klean Strip Strip-X which contains less methylene chloride, took four hours to remove two layers of the epoxy paint. The experimental and

Table 4. Results of paint remover screening showing the layers of oil-based alkyd and two-component oil-based epoxy removed on 1 month aged panels. Promising experimental formulations from this test were later validated on 1 year aged panels with competition.

Company	Paint Remover	Ingredients (MSDS)	Retail Cost (gallon)	Alkyd (5 Layers)					Epoxy (3 Layers)			
				5 min	15 min	30 min	1 hrs	4 hrs	15 min	30 min	1 hrs	4 hrs
W. M. Barr	Klean-Strip Aircraft Remover	methylene chloride/methanol/Tall oil/ammonium hydroxide/xylene	$27.99	5	5	5	5	5	2	2	2	2
	Klean-Strip Premium Stripper	methylene chloride/methanol/Stoddard solvent	$22.98	5	5	5	5	5	2	2	2	2
	Klean-Strip Strip-X Stripper	methylene chloride/methanol/toluene/acetone/xylene	$18.97		5	5	5	5				2
	Citristrip Safer Paint & Varnish Stripping Gel	NMP/DBE	$39.94				5	5				
	Experimental Formula A	toluene/acetone/methanol	$23.88*		5	5	5	5				
	Experimental Formula B	1,2 trans dichloroethylene/acetone/methanol	$42.97*		5	5	5	5				
	Experimental Formula C	1,3 dioxolane/acetone/methanol	$31.55*		5	5	5	5				
	Experimental Formula D	benzyl alcohol emulsion	$39.96*									
	Experimental Formula E	DBE emulsion	$34.00*									
Dumond	Peel Away 1	calcium hydroxide/magnesium hydroxide/sodium hydroxide/water	$68.30			1	3	5				
	Peel Away 5 Soy Based	benzyl alcohol/NMP/soya methyl ester/DBE/water	$78.12					5				
	Peel Away 7	benzyl alcohol/NMP/DBE/water	$90.15									
	Smart Strip	water/benzyl alcohol/water	$50.59									
	Smart Strip Pro	water/benzyl alcohol/formic acid/water	$77.74									
Ecoprocote	EcoFast HD Heavy Duty Paint Stripper	NMP/soy methyl ester/water	$54.99									
EZ Strip	EZ Strip Paint and Varnish Stripper	DBE/triethyl phosphate/water	$38.98									
Franmar	Soy-Gel Paint and Urethane Remover	NMP/DBE/soy ester/water	$81.20					5				
Motsenbocker	Lift Off Paint and Varnish Remover	acetone/2-butoxyethanol/DBE/water	$49.94									
Packaging Service Co.	Crown Paint Strip Next	DBE/DMSO/water	$47.92					5				
PPG	DuraPrep 200 Coating Remover (Gel)	benzyl alcohol\solvent naphtha/2-aminoethanol/nonylphenol, branched ethoxylated	$41.34					5				
	DuraPrep 240 Industrial Coating Remover (Gel)	benzyl alcohol/hydrogen proxide/solvent naphtha/glycollic acid/malic acid/barium bis(dinonylnaphthalenesuphonate)/amines, coco alkyl, ethoxylated	$40.75					5				
	DuraPrep Prep 400 Overspray Remover	benzyl alcohol/petroleum distillates/glycolic acid/quaternary ammonium compounds/hydrogen proxide/water	$127.60					5				
Solvent Kleene	D-Zolve 1012 Powder Coating Remover (immersion tank)	alkyl methyl ester/potassium hydroxide/cyclic amide/water	Not Available		1	2	2	5				
	D-Zolve 15-33R (aircraft)	alkyl methyl ester/petroleum naphtha/benzyl alcohol/methyl phenyl ether/water	Not Available					5				
Sunnyside	Multi-Strip Professional Paint Remover	DBE/NMP/formic acid/water	$49.97					5				
	Ready Strip Pro	DBE/NMP/formic acid/water	$39.97									
	Ready Strip Safer Paint & Varnish Remover	DBE/NMP/formic acid/water	$34.71									
	Ready-Strip Spray	NMP/DBE/monoethanolamine/water	$39.92									
	Ultri-Strip	DBE/NMP/formic acid/water	$66.85					5				
This Stuff Works, Inc.	TSW2 Multi-Master	NMP/DBE/water	$99.95					5				
	TSW2G Multi-Master (Gel)	NMP/DBE/water	$99.95					5				
	TSW3G (GEL) Mason-Master	potassium hydroxide/butyl cellosolve/water	$85.00			1	1	4				
	TSW9 Plasti-Master	DBE/proprietary surfactant/water	$99.95									
Zinsser	Magic Strip Citrus-Action	NMP/DBE/d-limonene/water	$84.32					5				

no layers of paint were removed with plastic paint scraper	
paint has softened requiring effort to remove with plastic scraper	
paint has blistered with all layers of paint removed with plastic scraper	

* Estimated retail price of experimental formulas based on formula, packaging, and manufacturing costs.

the commercial paint removers failed to strip any layers of the epoxy paint at 15 and 30 minutes, 1 hour and four hours.

Since the experimental formulas A, B, and C showed comparable efficacy on the 1 month aged alkyd painted board in comparison to the methylene chloride containing formulas they were allowed to advance onto the validation test done on a 1 year aged alkyd painted board.

Final Efficacy Validation of Experimental Formulations vs Competition on 1 Year Aged Boards

As shown in the results in Table 5, Klean Strip Premium Stripper took 15 minutes to remove all layers of paint on a 1 year aged panel but only 5 minutes on the newer 1 month aged panel. The alternate paint removers also required more time to strip all layers of the alkyd paint on the aged panels. The time to strip all layers increased to an hour compared to 30 minutes for the Experimental Formulas A, B, and C. Crown Safer Paint Strip stripped all layers of paint after 24 hours on the new panels but failed to remove any layers of paint on the 1 year aged panels. See **Appendix B** for a visual of 1 month and 1 year aged panels used in this validation test. The difference in results between the 1 month aged panels in Table 4 and Table 5 is due to the inconsistencies of how Alkyd paint cures over a month time. Experiments done in Table 4 were done with one month boards created on different time periods than used in table 5. As the alkyd painted panels age, the alkyd resin continues to crosslink making the paint more difficult to strip. More consistent results are obtained using alkyd painted panels which are aged for at least one year. 1 month aged panels are used strictly for directional feedback and should not be used to validate the final efficacy of a paint remover.

Table 5. Validation results of paint remover testing done on panels aged 1 month to 1 year. Since Alkyd paint continues to bond and get harder to remove over time, 1 year aged paint boards are more realistic on what the consumer will experience while paint stripping. Klean-strip Premium Stripper methylene chloride based stripper is far superior to the current competitive set on the market. New experimental formulas are extremely flammable and do not perform as fast as current methylene chloride formulations. The difference in results between the 1 month aged panels in Table 4 and Table 5 is due to the inconsistencies of how Alkyd paint cures over a month time. As the alkyd painted panels age, the alkyd resin continues to crosslink making the paint more difficult to strip. More consistent results are obtained alkyd painted panels which are aged for at least one year. 1 month aged panels are used strictly for directional feedback.

Paint Remover	Ingredients (MSDS)	Month Old Panel - Alkyd (5 Layers)						Year Old Panel - Alkyd (5 Layers)					
		5 min	15 min	30 min	1 hrs	4 hrs	24 hrs	5 min	15 min	30 min	1 hrs	4 hrs	24 hrs
Klean-Strip Premium Stripper	methylene chloride/methanol/Stoddard solvent	5	5	5	5				5	5	5		
Klean-Strip Strip-X Stripper	methylene chloride/methanol/toluene/acetone/xylene		1	5	5					5	5		
Experimental Formula A	toluene/acetone/methanol		1	5	5						5		
Experimental Formula B	1,2 trans dichloroethylene/acetone/methanol			5	5						5		
Experimental Formula C	1,3 dioxolane/acetone/methanol		1	5	5						5		
Citristrip Safer Paint & Varnish Stripping Gel	NMP/DBE					5	5					5	5
Peel Away 1	calcium hydroxide/magnesium hydroxide/sodium hydroxide					3	5					5	5
Smart Strip	water/benzyl alcohol						5						5
Smart Strip Pro	water/benzyl alcohol/formic acid			1	1	1	5						5
EZ Strip Paint and Varnish Stripper	DBE/triethyl phosphate												
Lift Off Paint and Varnish Remover	acetone/2-butoxyethanol/DBE												
Crown Safer Paint Strip	DBE/DMSO						5						

no layers of paint were removed with plastic paint scraper	
paint has softened requiring effort to remove with plastic scraper	
paint has blistered with all layers of paint removed with plastic scraper	

Test results comparing the performance of three methylene chloride paint removers to five experimental formulas and five commercial non-methylene chloride paint removers on an OEM automotive coating are listed in Table 6. The five commercial non-methylene chloride paint removers were formulated to remove automotive or aircraft coatings containing a blend of solvents and an activator. The effects on automotive coating was evaluated after 15, and 30 minutes, 1 hour and 4 hours. Only one of the paint removers tested, Klean Strip Aircraft Remover, stripped all layers of the OEM automotive coating. Klean Strip Aircraft Remover stripped the clear, color and base coat in 15 minutes and continued to strip all layers at 4 hours without drying. Klean Strip Aircraft Remover is formulated to remove automotive coatings containing methylene chloride and the activator ammonium hydroxide. Klean Strip Premium Stripper and Klean Strip Strip-X, removed the clear and color coat after 15 minutes but did not strip the primer coat after four hours. Klean Strip Premium Stripper and Klean Strip-X are methylene chloride paint removers but do not contain an activator. Experimental Formulas A, B, and C were also able to strip the clear and color coat after 15 minutes but failed to strip the primer coat after 4 hours. Experimental Formulas D and E failed to strip the automotive coating after four hours. D-Zolve 15-33R rom Solvent Kleene was the only commercial non-methylene chloride paint remover tested that stripped the automotive coating. D-Zolve 15-33R is a paint remover designed to remove aircraft coatings and took four hours to remove the clear and color coats.

Table 6. Results of paint remover testing on an OEM Automotive Coating.

Company	Paint Remover	Ingredients (MSDS)	Automotive Coating			
			15 min	30 min	1 hrs	4 hrs
W.M. Barr	Klean-Strip Aircraft Remover	methylene chloride/methanol/Tall oil/ammonium hydroxide/xylene				
	Klean-Strip Premium Stripper	methylene chloride/methanol/Stoddard solvent				
	Klean-Strip Strip-X Stripper	methylene chloride/methanol/toluene/nonyl phenol ethoxylate/acetone/xylene				
	Citristrip Safer Paint & Varnish Stripping Gel	NMP/DBE				
	Experimental Formula A	toluene/acetone/methanol				
	Experimental Formula B	1,2 trans dichloroethylene/acetone/methanol				
	Experimental Formula C	1,3 dioxolane/acetone/methanol				
	Experimental Formula D	benzyl alcohol emulsion				
	Experimental Formula E	DBE emulsion				
PPG	DuraPrep 200 Coating Remover (Gel)	benzyl alcohol\solvent naphtha/2-aminoethanol/nonylphenol, branched ethoxylated				
	DuraPrep 240 Industrial Coating Remover (Gel)	benzyl alcohol/hydrogen proxide/solvent naphtha/glycollic acid/malic acid/barium bis(dinonylnaphthalenesuphonate)/amines, coco alkyl, ethoxylated				
	DuraPrep Prep 400 Overspray Remover	benzyl alcohol/petroleum distillates/glycolic acid/quaternary ammonium compounds/hydrogen proxide				
Solvent Kleene	D-Zolve 1012 Powder Coating Remover (immersion tank)	alkyl methyl ester/potassium hydroxide/cyclic amide				
	D-Zolve 15-33R (aircraft)	alkyl methyl ester/petroleum naphtha/benzyl alcohol/methyl phenyl ether				

No effect	
Stripped clear coat and top coat	
Stripped clear coat, top coat and base coat	

Conclusion

The performance of methylene chloride was compared to 22 alternate solvents selected as possible replacements for methylene chloride in paint removers. Testing was conducted on three types of paints using wood panels painted with an oil-based alkyd paint, wood panels paint with a two-component oil-based epoxy paint and an OEM automotive coating. Trans-1,2-dichloroethylene and 1,3-dioxolane were

identified as the best performing alternate solvent tested. However, based on the results from this study, none of the alternative solvents tested were determined to be an adequate replacement for methylene chloride.

Based on the results of the solvents screening testing, two solvents, trans-1,2-dichloroethylene and 1,3-dioxolane were selected as having some paint remover potential and were formulated into paint removers that met the 50 wt% VOC limit for paint removers. Three other experimental formulas were also formulated based on a toluene, methanol and acetone formula, a benzyl alcohol emulsion formula and a DBE emulsion formula. Three methylene chloride paint removers were then compared to the five-experimental formula and 26 commercially available non-methylene chloride paint removers. Based on the results of the paint remover study, none of the experimental formulas or the 26 non-methylene chloride paint removers were determined to be an adequate replacement for methylene chloride paint removers. Performance of the experimental formulas based on trans-1,2-dichloroethylene and 1,3-dioxolane was determined to be no better than the experimental formula based on toluene, methanol and acetone.

Methylene chloride has been the preferred for use in paint removers for seventy. Consumers expect that paint removers to be able to remove many types of coatings, remove multiple layers of the coating and to start working within 15 minutes and quickly remove the coating. To be an effective paint remover, the solvent must be able to penetrate multiple layers of paint and have solubility to cause the paint to swell which breaks the bond of the paint to the substrate. The size of the solvent molecule and the polarity of the molecule affects rate the solvent penetrates the coating. The movement of the solvent from the paint remover to the paint layer is call diffusion and is the result of the random kinetic movement of the solvent molecules. Smaller, nonpolar molecules will have a higher diffusion rate into the coating than molecules that are larger or more polar. The more effective replacements for methylene chloride will be molecules with the following general characteristics, small polar or halogenated molecules, five-member cyclic rings or six-member aromatic rings. Unlike methylene chloride, these types of molecules are most likely flammable and possibly will have a significant threat to health and safety.

Appendix A. Composition of Paint Removers and Flash Point as Listed in Material Safety Data Sheets

Company	Paint Remover	Ingredients (MSDS)			Flash Point
		Chemical Name	CAS Number	Weight %	
W. M. Barr	**Klean Strip Aircraft Remover**	methylene chloride	75-09-2	60 – 100	no flash to boiling
		methanol	67-56-1	5 – 10	
		ammonium hydroxide	1336-21-6	< 5	
		xylene	1330-20-7	< 5	
		hydrotreated light distillate (petroleum)	64742-47-8	< 5	
		fatty acid soap	68132-50-3	< 5	
		ethylbenzene	100-41-4	< 3	
	Klean Strip Premium Stripper	methylene chloride	75-09-2	60 – 100	no flash to boiling
		methanol	67-56-1	10 – 20	
		Stoddard Solvent	8052-41-2	< 5	
	Klean Strip Strip-X Stripper	methylene chloride	75-09-2	30 – 40	30°F
		methanol	67-56-1	15 – 26	
		acetone	67-64-1	< 10	
		xylene	1330-20-7	< 10	
		toluene	108-88-3	< 10	
		ethylbenzene	100-41-4	< 5	
		ethyl alcohol	64-17-5	< 5	
		isopropyl alcohol	67-63-0	< 5	
	Citristrip Stripping Gel	n-methyl-2-pyrrolidone	872-50-4	30 – 60	>200°F
		dimethyl adipate	627-93-0	10 – 30	
		dimethyl glutarate	1119-40-0	10 – 20	
	Experimental Formula A	acetone	67-64-1	40 – 50	0°F
		toluene	108-88-3	40 – 50	
		methanol	67-56-1	< 10	
	Experimental Formula B	acetone	67-64-1	40 – 50	0°F
		trans-1,2-dichloroethylene	646-06-0	40 – 50	
		methanol	67-56-1	< 10	
	Experimental Formula C	acetone	67-64-1	45 – 55	0°F
		1,3-dioxolane	646-06-0	40 – 50	
		methanol	67-56-1	< 10	
	Experimental Formula D	benzyl alcohol	100-51-6	20 - 40	no flash to boiling
		alcohol ethoxylate (alcohols, c9-11, ethoxylated)	68439-46-3	< 5	
	Experimental Formula E	water	7732-15-5	40 – 60	no flash to boiling
		dimethyl adipate	627-93-0	10 – 30	
		dimethyl glutarate	1119-40-0	10 – 20	
		starch	9005-25-8	5 – 20	
		alcohol ethoxylate (alcohols, C9-11, ethoxylated)	68439-46-3	<5	

Company	Paint Remover	Ingredients (MSDS)			Flash Point
		Chemical Name	CAS Number	Weight %	
Dumond	Peel Away 1	calcium hydroxide	1305-62-0	21	none
		magnesium hydroxide	1309-42-8	16	
		sodium hydroxide	1310-73-2	9	
	Peel Away 5 Soy Based	benzyl alcohol	100-51-6	20 – 50	> 200°F
		n-methyl-2-pyrrolidone	872-50-4	25 – 35	
		fatty acid methyl ester	67784-80-9	15 – 20	
		alpha-(4-nonylphenyl)-omega-hydroxy-poly(oxy-1,2,ethanediyl) branched	127087-0	< 3	
		dimethyl glutarate	1119-40-0	25 – 35	
		dimethyl adipate	627-93-0		
	Peel Away 7	benzyl alcohol	100-51-6	20 – 40	> 200°F
		n-methyl-2-pyrrolidone	872-50-4	10 – 20	
		alpha-(4-nonylphenyl)-omega-hydroxy-poly(oxy-1,2,ethanediyl) branched	127087-0	< 2	
		dimethyl glutarate	1119-40-0	25 – 35	
		dimethyl adipate	627-93-0		
	Smart Strip	water	7732-18-5	40 – 60	none
		benzyl alcohol	100-51-6	30 – 50	
		titanium dioxide	13463-67-7	1 - 5	
	Smart Strip Pro	water	7732-18-5	40 – 60	none
		benzyl alcohol	100-51-6	30 – 50	
		titanium dioxide	13463-67-7	1 – 5	
		formic acid	64-18-6	1 – 5	
Ecoprocote	EcoFast HD Heavy Duty Paint Stripper	water	7732-18-5	Trade Secret	non-flammable
		benzyl alcohol	100-51-6	Trade Secret	
		Bio-Based Emulsion	Non-Hazardous	Trade Secret	
		Solvent-Free Thickeners	Non-Hazardous	< 1	
		Solvent-Free Surfactants	Non-Hazardous	1 – 5	
EZ Strip	EZ Strip Paint and Varnish Stripper	dimethyl adipate	627-93-0	3 – 7	not listed
		dimethyl succinate	106-65-0	5 – 10	
		dimethyl glutarate	1119-40-0	10 – 30	
		triethyl phosphate	78-40-0	3 – 7	
Frammar	Soy-Gel Paint and Varnish Stripper	n-methyl-2-pyrrolidone	872-50-4	41	> 200°F
		dimethyl adipate	627-93-0	40 – 45	
		dimethyl glutarate	1119-40-0		
		soy ester	67781-80-9	15 – 20	
		Proprietary Thickening and Surfactant Blend	Proprietary	1 – 5	
Motsenbocker	Lift Off Paint and Varnish Remover	acetone	67-64-1	< 10	not listed
		2-butoxy ethanol	111-76-2	Not Listed	
		dimethyl adipate	627-93-0	Not Listed	
		dimethyl succinate	106-65-0	Not Listed	
		dimethyl glutarate	1119-40-0	Not Listed	

Company	Paint Remover	Ingredients (MSDS)			Flash Point
		Chemical Name	CAS Number	Weight %	
Packaging Services Co	**Crown Paint Strip Next**	dimethyl sulfoxide	67-68-5	20 – 25	160°F
		dimethyl glutarate	1119-40-0	45 – 45	
		dimethyl succinate	106-65-0	10 – 20	
		dimethyl adipate	627-93-0	5 – 15	
		alcohol ethoxylate surfactant	Not Listed	0 – 1	
PPG	**DuraPrep 200 Coating Remover**	benzyl alcohol	100-51-6	15 – 40	221°F
		solvent naphtha (petroleum), light aromatic	64742-95-6	1 – 5	
		2-aminoethanol	141-43-5	1 – 5	
		nonylphenol, branched, ethoxylated	68412-54-4	0.1 – 1	
	DuraPrep 240 Industrial Coating Remover	benzyl alcohol	100-51-6	15 – 40	178°F
		hydrogen peroxide	7722-84-1	5 – 10	
		solvent naphtha (petroleum), heavy aromatic	64742-94-5	3 – 7	
		barium bis(dinonyl-naphthalenesulphonate)	25619-56-1	0.1 – 1	
		amines, coco alkyl, ethoxylated	61791-14-8	0.1 – 1	
	DuraPrep Prep 400 Overspray Remover	2-(methoxymethylethoxy) propanol	34590-94-8	30 – 60	203°F
		dimethyl sulfoxide	67-68-5	7 – 13	
		dimethyl glutarate	1119-40-0	5 – 10	
		benzyl alcohol	100-51-6	5 – 10	
Solvent Kleene	**D-Zolve 1012 Power Coating Remover**	alkyl methyl ester	Proprietary	Trade Secret	170°F
		potassium hydroxide	1310-58-3	2 – 5	
		cyclic amide	72-50-4	5 – 30	
Sunnyside	**Multi-Strip Professional Paint Remover**	n-methyl-2-pyrrolidone	872-50-4	15 – 35	203°F
		dimethyl glutarate	1119-40-0	20 – 35	
		dimethyl adipate	627-93-0	5 – 10	
		dimethyl succinate	106-65-0	5 – 15	
		formic acid	64-18-6	1 – 2	
		non-hazardous components	N/A	20 – 40	
	Ready Strip Pro	benzyl alcohol	100-51-6	20 – 35	205°F
		n-methyl-2-pyrrolidone	872-50-4	5 – 15	
		formic acid	64-18-6	2 – 15	
		non-hazardous components	N/A	50 – 65	
	Ready Strip Safer Paint & Varnish Remover	benzyl alcohol	100-51-6	20 – 35	205°F
		n-methyl-2-pyrrolidone	872-50-4	5 – 15	
		formic acid	64-18-6	2 – 15	
		non-hazardous components	N/A	50 – 65	
	Ready Strip Spray	n-methyl-2-pyrrolidone	872-50-4	35 – 50	205°F
		dimethyl glutarate	1119-40-0	20 – 35	
		dimethyl adipate	627-93-0	5 – 20	
		dimethyl succinate	106-65-0	3 – 5	
		monoethanolamine	141-43-5	1 – 3	
		isopropanolamine mixture	78-96-6 110-97-4 122-20-3	2 - 5	
		non-hazardous components	N/A	45 – 50	

Company	Paint Remover	Ingredients (MSDS)			Flash Point
		Chemical Name	CAS Number	Weight %	
Sunnyside	Ready Strip Spray	n-methyl-2-pyrrolidone	872-50-4	35 – 50	205°F
		dimethyl glutarate	1119-40-0	20 – 35	
		dimethyl adipate	627-93-0	5 – 20	
		dimethyl succinate	106-65-0	3 – 5	
		monoethanolamine	141-43-5	1 – 3	
		isopropanolamine mixture	78-96-6	2 - 5	
			110-97-4		
			122-20-3		
		non-hazardous components	N/A	45 – 50	
	Ultra-Strip	n-methyl-2-pyrrolidone	872-50-4	35 – 50	>200°F
		dimethyl glutarate	119-40-0	20 – 35	
		dimethyl adipate	627-93-0	5 – 20	
		dimethyl succinate	106-65-0	3 – 5	
		formic acid	64-18-6	1 – 2	
		non-hazardous components	N/A	5 – 35	
This Stuff Works, Inc	TSW2 Multi-Master	n-methyl-2-pyrrolidone	872-50-4	Trade Secret	>212°F
		dimethyl glutarate	1119-40-0	Trade Secret	
		dimethyl adipate	627-93-0	Trade Secret	
	TSW2G Multi-Master (Gel)	n-methyl-2-pyrrolidone	872-50-4	Trade Secret	>212°F
		dimethyl glutarate	1119-40-0	Trade Secret	
		dimethyl adipate	627-93-0	Trade Secret	
	TSW3G (Gel) Mason-Master	potassium hydroxide	1310-58-3	Trade Secret	non-flammable
		butyl cellosolve	11-76-2	Trade Secret	
	TSW9 Plasti-Master	dimethyl glutarate	1119-40-0	Trade Secret	>212°F
		dimethyl adipate	627-93-0	Trade Secret	
		proprietary surfactant	Trade Secret	Trade Secret	
Zinsser	Magic Strip Citrus-Action	n-methyl-2-pyrrolidone	872-50-4	25 – 50	>199°F
		dimethyl glutarate	1119-40-0	25 – 50	
		dimethyl adipate	627-93-0	2.5 – 10	
		dimethyl succinate	106-65-0	2.5 – 10	
		monoethanolamine	141-43-5	2.5 – 10	
		d-limonene	5989-27-5	1.0 – 2.5	

Appendix B: Photographs comparing test results on new and aged panels painted with an oil-based alkyd paint.

Figure 1. Results of stripping screening test on a new panel **(1-month-aged)** painted with an oil-based alkyd paint. **Column 1** is Klean Strip Premium (methylene chloride based), **Column 2** is Strip-X methylene chloride based (lower level), **Column 3** is an experimental formula containing toluene, **Column 4** is an experimental formula containing trans-1,2-dichloroethylene, **Column 5** is an experimental formula containing 1,3-dioxolane and **Column 6** is Citrus strip (contains NMP and DBE). Blue = 1st paint layer applied, White = 2nd paint layer applied, Green = 3rd paint layer applied, Yellow = 4th paint layer applied, Red= last paint layer applied. Seeing Red = no layers of paint were stripped.

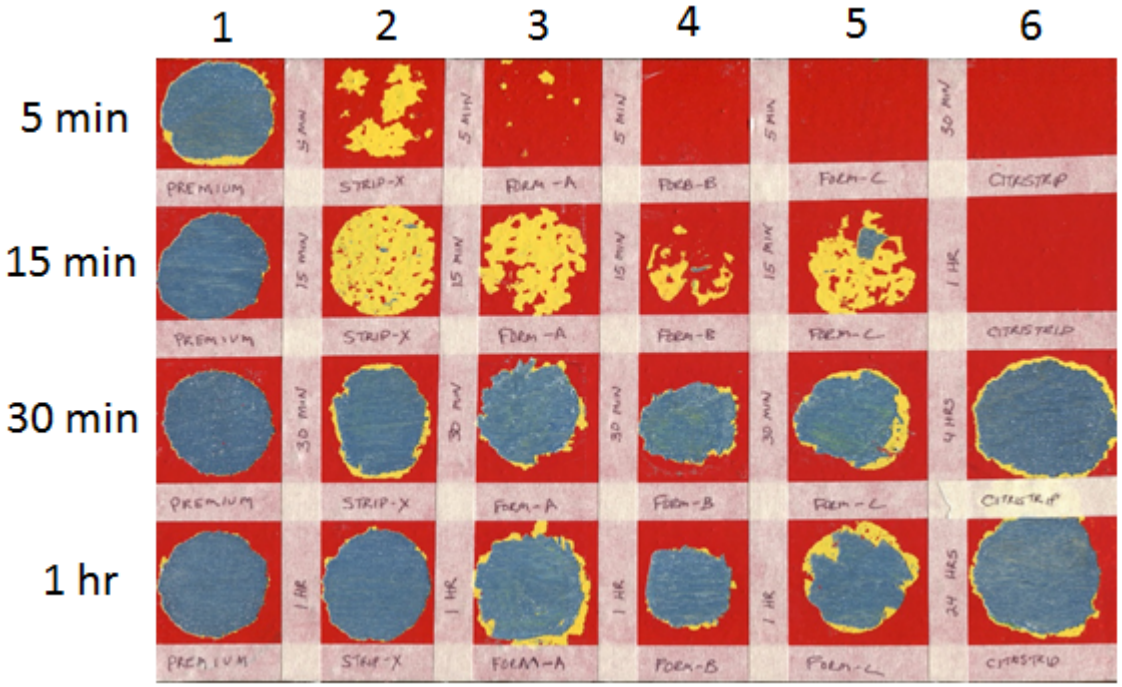


Figure 2. Results of stripping validation test on an aged panel **(1-year-aged)** painted with an oil-based alkyd paint. **Column 1** is Klean Strip Premium (methylene chloride based), **Column 2** is Strip-X methylene chloride based (lower level), **Column 3** is an experimental formula containing toluene, **Column 4** is an experimental formula containing trans-1,2-dichloroethylene, **Column 5** is an experimental formula containing 1,3-dioxolane and **Column 6** is Citrus strip (contains NMP and DBE). Blue = 1st paint layer applied, White = 2nd paint layer applied, Green = 3rd paint layer applied, Yellow = 4th paint layer applied, Red= last paint layer applied. Seeing Red = no layers of paint were stripped.

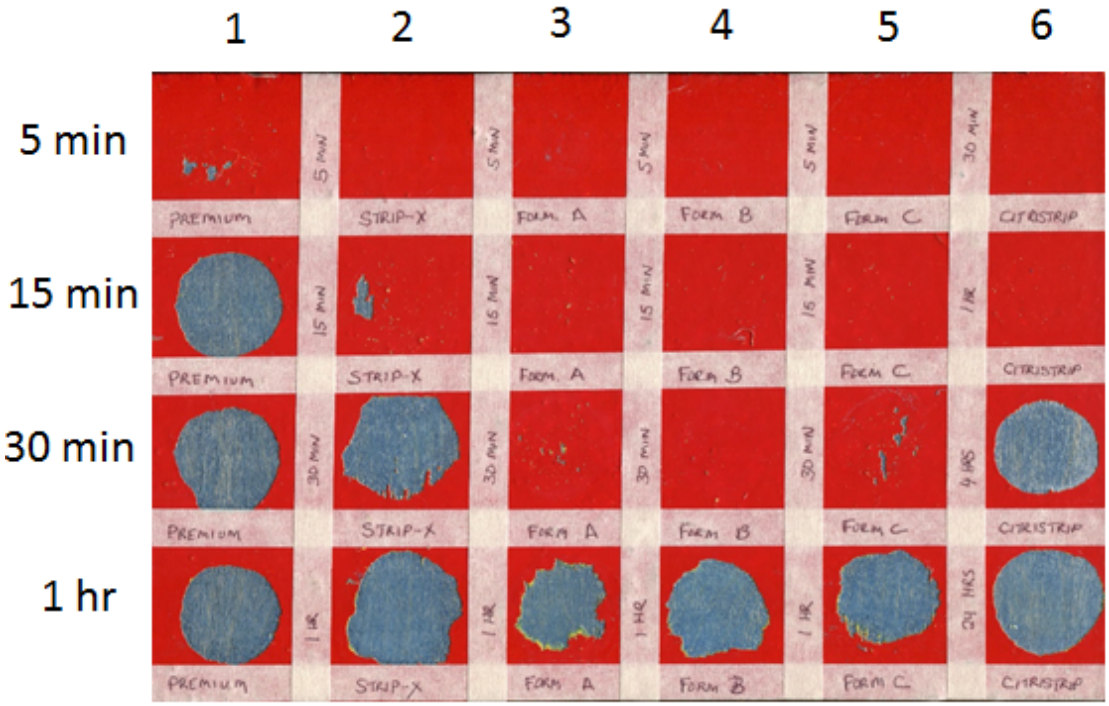


Figure 3. Results of stripping screening test on a new panel **(1-month-aged)** painted with an oil-based alkyd paint**. Column 1** is Peel Away 1 (caustic based), **Column 2** is Smart Strip (benzyl alcohol based), **Column 3** is Smart Strip Pro (benzyl alcohol based with formic acid), **Column 4** is EZ strip (DBE and triethyl phosphate), **Column 5** Lift Off (acetone and 2-butoxy ethanol and DBE based) and **Column 6** is Safer Paint Strip (DMSO and DBE based). Blue = 1st paint layer applied, White = 2nd paint layer applied, Green = 3rd paint layer applied, Yellow = 4th paint layer applied, Red= last paint layer applied. Seeing Red = no layers of paint were stripped. ** Ingredients of competitive products cited from MSDS and/or GC analysis.

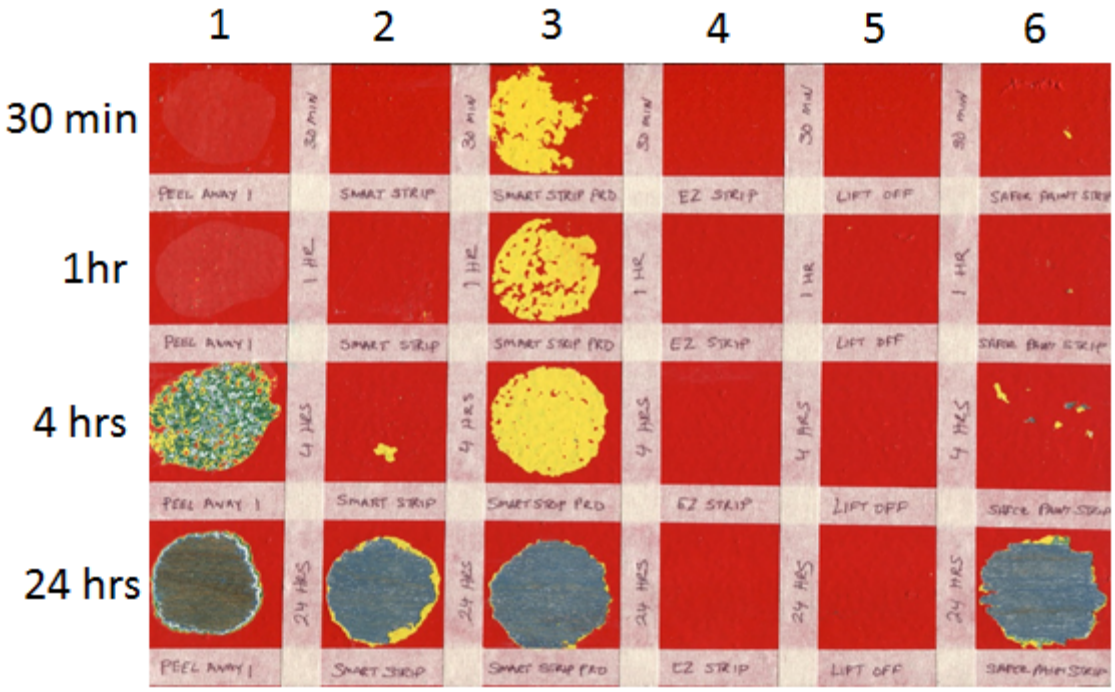
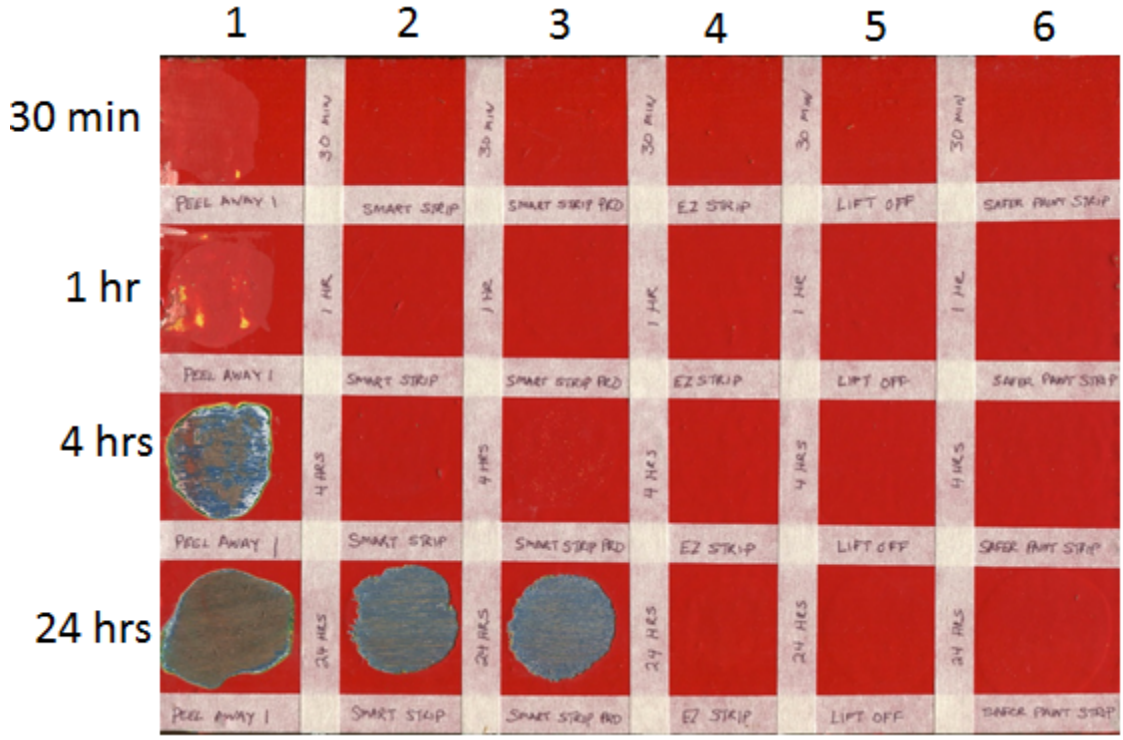


Figure 4. Results of stripping validation test on an aged panel **(1-year-aged)** painted with an oil-based alkyd paint. **Column 1** is Peel Away 1 (caustic based), **Column 2** is Smart Strip (benzyl alcohol based), **Column 3** is Smart Strip Pro (benzyl alcohol based with formic acid), **Column 4** is EZ strip (DBE and triethyl phosphate), **Column 5** Lift Off (acetone and 2-butoxy ethanol and DBE based) and **Column 6** is Safer Paint Strip (DMSO and DBE based). Blue = 1st paint layer applied, White = 2nd paint layer applied, Green = 3rd paint layer applied, Yellow = 4th paint layer applied, Red= last paint layer applied. Seeing Red = no layers of paint were stripped. ** Ingredients of competitive products cited from MSDS and/or GC analysis.



Authors

Matthew M. Petkus is the Director of Research and Development at W.M. Barr and is an expert in studying the product usage habits of consumers. During his career of working in the CPG industry, Matt has traveled and studied the consumer product usage habits in Argentina, Italy, Japan, UK, China, Germany, and in the USA. Most recently at W.M. Barr, Matt has participated in an ethnography study in the USA focused on observing consumer use habits of paint stripper products. Matt holds his PhD and Master's Degree in Chemistry from Arizona State University. Matt received his Bachelor of Science in Chemistry from the University of Wisconsin-Whitewater. Most recently, Matt received his Master's degree in Product Development and Design Management from Northwestern University.

Timothy G. Teague is a Senior Research & Development Chemist at W.M. Barr and is responsible for developing new products for the consumer market. During his thirty-year career, he has worked as a Research & Development Chemist formulating new consumer and industrial products and as a Quality Assurance Chemist supporting manufacturing activities. As a Research & Development Chemist, he has formulated a wide range of new consumer and industrial products including coatings for exterior wood, kitchen cabinet stains, paint removers, thinners for coatings, and cleaning and other products. Tim has a Bachelor of Science in Chemical Engineering from the University of Arkansas at Fayetteville.